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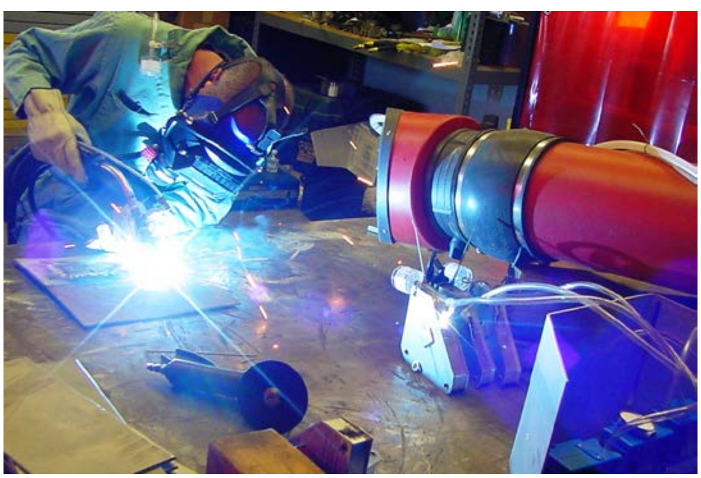
COST AND PERFORMANCE REPORT:

INNOVATIVE WELDING TECHNOLOGIES USING SILICON ADDITIVES TO CONTROL HAZARDOUS AIR POLLUTANT (HAP) EMISSIONS



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14. ABSTRACT
The welding process results in the formation of high concentrations of nano-sized particles loaded with toxic metals such as hexavalent chromium (Cr^{6+}), nickel (Ni), and manganese (Mn). Welding fumes pose serious health risks to welders because fumes can cause respiratory and neurological ailments as well as cancer. Tightened occupational standards require an exposure reduction of at least 90% that is not satisfied by current control technologies. There is also potential public concern about the environmental risks associated with the release of welding fumes into ambient air.

The overall objective of this demonstration was to develop an innovative silica precursor technology that can limit the oxidation of chromium by quenching oxygen species and coating metal particles in welding fumes with a thin, amorphous silica layer. An additional objective was to assess the benefit of increased particle size distribution. The demonstration verified the feasibility and practicality of implementing silica precursor technology into DOD welding operations.

Silica precursor technology was demonstrated to be an effective means of controlling metal emissions in welding fumes. The two-fold approach of limiting oxidation potential and coating metal particles with an amorphous silica layer goes beyond previous control technologies by addressing all the toxic metals, regardless of their oxidation state. This project demonstrated, through both a laboratory study and field tests, the benefits of adding silica precursor during the welding process.

15. SUBJECT TERMS
Welding, vapor-phase silica precursor, shielding gas additive, Tetramethylsilane (TMS)

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LIST OF ACRONYMS AND SYMBOLS

Al	aluminum
ANOVA	analysis of variance
APE	ammunition peculiar equipment
Ar	arsenic
ASTM	American Society for Testing and Materials
atm	atmospheric
a.u.	arbitrary unit
AWM	all weld metal
AWS	American Welding Society
BP	base plate
CARB	California Air Resources Board
Cd	cadmium
CFU	colony forming unit
CFH	cubic feet per hour
Co	cobalt
Cr	chromium
Cr^{6+}	hexavalent chromium
Cu	copper
DOD	Department of Defense
ECM	formerly, Environmental Cost Management Company
ELPI	electrical low pressure impactor
EPA	environmental Protection Agency
Fe	iron
GMAW	gas metal arc welding

GTAW	gas tungsten arc welding
HAP	hazardous air pollutant
HAZ	heat affected zone
HF	hydrofluoric acid
IC	ion chromatography
ICP-AES	inductively coupled plasma-atomic emission spectroscopy
IDST	insulated double shroud torch
Ipm	inches per minute
KIGAM	Korean Institute of Geoscience and Mineral Resources
ksi	kilo (1,000) pounds per square inch
LEV	local exhaust ventilation
LFL	lower flammable limit
LLC	lethal logarithmic concentrations
Lpm	liters per minute
MAIC	Majority Analytical Instrument Center
mg/L	milligrams per liter
MIG	metal inert gas
mm	millimeters
Mn	manganese
ms	millisecond
NESHAP	National Emission Standards for Hazardous Air Pollutants
Ni	nickel
NIOSH	National Institute for Occupational Safety and Health
NO	nitric oxide
nm	nanometers

OSHA	Occupational Safety and Health Administration
Pb	lead
PEL	permissible exposure limit
PERC	Particle Engineering Research Center
PPE	personal protective equipment
PTFE	polytetrafluoroethylene (teflon)
PVC	polyvinyl chloride
REL	recommended exposure limit
SCE	silica coating efficiency
SiO_2	silicon dioxide
SMAW	shielded metal arc welding
SMPS	scanning mobility particle sizer
SOP	standing operating procedure
TEAD	Tooele Army Depot
TEM	transmission electron microscopy
TEOS	tetraethyloxysilane
TMS	tetramethylsilane
TWA	time weighted average
UTS	ultimate tensile strength
WM	weld metal
XPS	x-ray photoelectron spectroscopy
YS	yield strength
Zn	zinc

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EXECUTIVE SUMMARY

OBJECTIVES OF THE DEMONSTRATION

The welding process results in the formation of high concentrations of nano-sized particles loaded with toxic metals such as hexavalent chromium (Cr6+), nickel (Ni), and manganese (Mn). Welding fumes pose serious health risks to welders because fumes can cause respiratory and neurological ailments as well as cancer. Tightened occupational standards require an exposure reduction of at least 90% that is not satisfied by current control technologies. There is also potential public concern about the environmental risks associated with the release of welding fumes into ambient air.

The overall objective of this demonstration was to develop an innovative silica precursor technology that can limit the oxidation of chromium by quenching oxygen species and coating metal particles in welding fumes with a thin, amorphous silica layer. An additional objective was to assess the benefit of increased particle size distribution. The demonstration verified the feasibility and practicality of implementing silica precursor technology into DOD welding operations.

TECHNOLOGY DESCRIPTION

Silica precursor technology has been demonstrated to be an effective means of controlling metal emissions in welding fumes. The two-fold approach of limiting oxidation potential and coating metal particles with an amorphous silica layer goes beyond previous control technologies by addressing all the toxic metals, regardless of their oxidation state. This project demonstrated, through both a laboratory study and field tests, the benefits of adding silica precursor during the welding process.

DEMONSTRATION RESULTS

The laboratory study showed that use of an insulated double-shroud torch (IDST) to inject vapor-phase silica precursor tetramethylsilane (TMS) into the welding operation reduced Cr^{6+} exposure by over 90% and satisfied the OSHA permissible exposure limit of 5 $\mu g/m^3$. The calculated silica coating efficiencies gave quantitative evidence of the encapsulation of metals inside the silica shell, and the transmission electron microscopy (TEM) images provided visual evidence. Scanning mobility particle sizer (SMPS) data showed the particle size distribution shifted to a larger size range, and the mode size of fume particles increased to 180~300 nm from 20 nm. The *Escherichia coli (E. coli)* study provided a preliminary result supporting the reduced biotoxicity of welding fume particles using the novel silica precursor technology.

The results of the field study further confirmed the capability of this technology to reduce Cr^{6+} and to encapsulate toxic metals such as Mn, Ni, and Cr. Two different sampling approaches were used in the field demonstration (low- and high-flow samplings). The results from the low-flow sampling were limited due to insufficient fume mass collection. The concentration of Cr^{6+} in most samples was lower than OSHA permissible exposure limit (PEL) (5 $\mu g/m^3$) in most samples, regardless of whether they were baseline or TMS-injected samples. The variation between samples was relatively large (Coefficient of Variance > 1). However, reduction of Cr^{6+}

and other metals by TMS technology was still observed through use of the statistical method Analysis of Variance (ANOVA). The results of high-flow sampling clearly showed the silica precursor technology was capable of reducing Cr^{6+} exposure below the OSHA PEL with > 90% Cr^{6+} reduction efficiency, and resulted in about 31.8% of the metals by mass sealed inside the silica shell.

Information extracted from interviews with welders in the field showed the use of TMS had no significant impact on welding operations. While TMS technology does not significantly deteriorate the mechanical quality of the welds, optimization of the different parameters to achieve the expected mechanical tensile parameters will be helpful. The cost assessment showed that use of TMS mixed at the nozzle and commercially available TMS cylinder gas did not significantly increase the overall cost of the welding operation. Also, it could potentially reduce the costs of retrofitting ventilation systems needed to meet new OSHA regulations.

IMPLEMENTATION ISSUES

One implementation issue considered was the safe handling of the TMS. A worst-case scenario was used to estimate the maximum possible TMS concentration. The TMS concentration in the case of a complete leak was still lower than the safety threshold value. In addition, there were no incidents caused by the TMS additive during the laboratory study and field demonstration.

The mechanical quality test suggested there is room for improving the TMS technology to achieve a higher weld quality. The weld qualities resulting from both baseline and TMS technology were lower than the minimum required by the standard for uniform metals, indicating that problems could have been partially due to welder error. Because this project was unexpectedly terminated before optimization and improvement could be achieved, the technology transfer will have to take a different path, which is currently being planned.

1.0 INTRODUCTION

1.1 BACKGROUND

Welding is a common repair and maintenance operation throughout the services at DOD depots and shipyards. It uses mild or stainless steel filler material to join pieces of metal. The intense energy expended in the welding process results in the formation of high concentrations of nano-sized particles loaded with hexavalent chromium (Cr^{6+}), nickel (Ni), manganese (Mn), and other toxic metals [1-5]. Hexavalent chromium and Ni are known human carcinogens [6], while exposure to Mn can cause serious adverse neurological effects, including a Parkinson's-like disorder known as manganism [7, 8]. Approximately 85% of the particles by mass are less than 1 µm in diameter, indicating that most fume particles are respirable and are able to travel deeply into the respiratory system and interact with human cells [9]. Hence, the welding process poses serious health risks to welders from inhalation of the welding fumes. The welding fume characteristics, as well as weld quality, are affected by parameters such as current, voltage, and shielding gas flow rate and composition [1, 10-12]. The complexity of the process creates a challenge for welder safety. Currently, the DOD spends approximately $36 million a year on personal protective equipment (PPE) for welding operations. In addition, welding fumes are also released into the atmosphere during the operations. While these hazardous air pollutants (HAPs) are usually not directly reported to the Environmental Protection Agency (EPA), facilities estimate the residual risk to public health. In certain states such as California [13], when the cancer risk exceeds a threshold of one in a million, facilities must report the findings to the public. When the threshold is exceeded, the facility is also expected to initiate measures to reduce the fugitive emissions.

Various welding fume control technologies have been developed in attempts to address the welding fume issues, such as using shielding gas to limit the oxidation of metals by preventing the penetration of reactive oxygen species [12] and reducing the fume generation rate [14]. Local exhaust ventilation (LEV) technology is available to remove fume particles from the welder's breathing zone [15, 16], but it is inconvenient and ineffective in field welding, where the movements of the welder are more frequent than during stationary welding [10]. The addition of reducing reagents such as methane or nitric oxide (NO) to shielding gas can consume oxygen species in the welding fume and hence limit formation of Cr^{6+} [17]. Similarly, the addition of reactive metals such as zinc (Zn) or aluminum (Al) to welding filler materials can reduce Cr^{6+} formation [18]. However, those technologies are either expensive, inconvenient, ineffective, or they create new hazards. Furthermore, the mechanical profiles of welds produced under those technologies have not yet been validated.

In summary, there are currently no effective technologies for welding fume control or respiratory protection. A well-balanced and feasible technology is critically needed to meet the following requirements:

- Better protection of DOD welders' health and safety
- Satisfaction of the occupational standards
- Reduction of the tremendous medical costs associated with the welding fume exposure
- Reduction of the residual risk associated with the release of HAPs into the atmosphere

1.2 OBJECTIVES OF THE DEMONSTRATION

The demonstration used the novel silica precursor technology to reduce the amount and toxicity of HAPs in the fume generated from the welding process, and to advance the research results from laboratory scale to DOD practice. Specifically, the demonstration strived to achieve the following objectives:

- Develop an innovative welding technology that allows optimal introduction of silica precursor to maximize the reduction of HAPs in welding fume
- Evaluate the performance of this new system in minimizing metal oxidation, encapsulating fume particles, and increasing fume particle size
- Evaluate the impact of changes induced by the silica precursor on the weld's mechanical properties
- Assess the operating costs for implementation

1.3 REGULATORY DRIVERS

DOD facility operating permits (Title V and Synthetic Minor Permits) require that facilities identify new technologies to reduce emissions and public health impacts. A significant portion of the health risks in DOD and heavy manufacturing are attributable to welding and metal-cutting emissions (such fumes are rich in metals with high toxicity). DOD facilities comply with HAP emissions regulations cited under National Emission Standards for Hazardous Air Pollutants (NESHAP). Welding operations for DOD shipbuilding and military equipment repair depots require HAP emissions reporting under expanding residual risk regulations. If the residual risk for a source category does not protect public health with an ample margin of safety, the EPA must promulgate health-based standards to further reduce HAP emissions.

Welding emission control is also required to meet tightening occupational exposure standards. For instance, the Occupational Safety and Health Administration (OSHA) lowered the 8-hour time-weighted average (8-hr TWA) PEL of Cr^{6+} from 52 $\mu g/m^3$ to 5 $\mu g/m^3$ in 2006 [19]. The National Institute for Occupational Safety and Health (NIOSH) also proposed an 8-hr TWA recommended exposure limit (REL) of 0.2 $\mu g/m^3$[20]. In 2009, NIOSH recommended all reasonable efforts should be made to reduce exposure to Cr^{6+} compounds below the REL through the use of work practice and engineering controls [21]. For nickel, the 8-hr TWA PEL is 1 mg/m^3, although the NIOSH REL is 0.015 mg/m^3. For manganese, the OSHA 8-hr TWA PEL is 5 mg/m^3 and the NIOSH REL is 1 mg/m^3.

2.0 DEMONSTRATION TECHNOLOGY

2.1 TECHNOLOGY DESCRIPTION

Silica precursor technology applied during welding feeds a minute amount of vapor-phase silica precursor into the welding shielding gas. The silica precursor scavenges oxygen species during oxidation, thus suppressing the oxidation of Cr. Silica coating occurs through the condensation of *in-situ*-generated amorphous silica onto metal particles. This scavenging and coating minimizes the subsequent oxidation encountered in the regular welding process. The amorphous silica layer insulates the metal species from human organisms when inhaled. Silica formed from this reaction also yields an amorphous web that effectively increases the size of metal particles. Figure 1 illustrates the mechanisms of the silica precursor technology.

To introduce the silica precursor tetramethylsilane (TMS) vapor into the welding arc zone, minimal modification to existing welding equipment is required. Experiments sponsored by the California Air Resources Board (CARB) demonstrated a > 61% reduction in Cr^{6+} formation, and the reduction could be further improved by optimizing the feeding condition. Experiments sponsored by the Korea Institute of Geoscience and Mineral Resources (KIGAM) were conducted at the University of Florida using tetraethylorthosilicate (TEOS)-added shielding gas in gas tungsten arc welding (GTAW). Experimental results showed an approximately 45% reduction of Cr^{6+}. Nitrate concentration also decreased by 53%, indicating that reactive oxygen species were also reduced. Transmission electron microscopy (TEM) images of collected fume aerosols showed silicon dioxide (SiO_2) coating on metal particles, verifying the efficacy of the proposed mechanism.

2.2 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

The advantages of the silica precursor technology include but are not limited to the following:

- The products from silica precursor decomposition are amorphous silica, carbon dioxide, and water, with no introduction of new hazards
- The technology is not metal specific, so it reduces the toxicity of all the metals regardless of oxidation state
- The technology does not alter the welding operation or require specific welding parameters, so only minimal training of the welder is required

The limitations of the technology include the requirement for minimal welding equipment modification, and the initial capital cost and the cost of consumables (i.e., TMS).

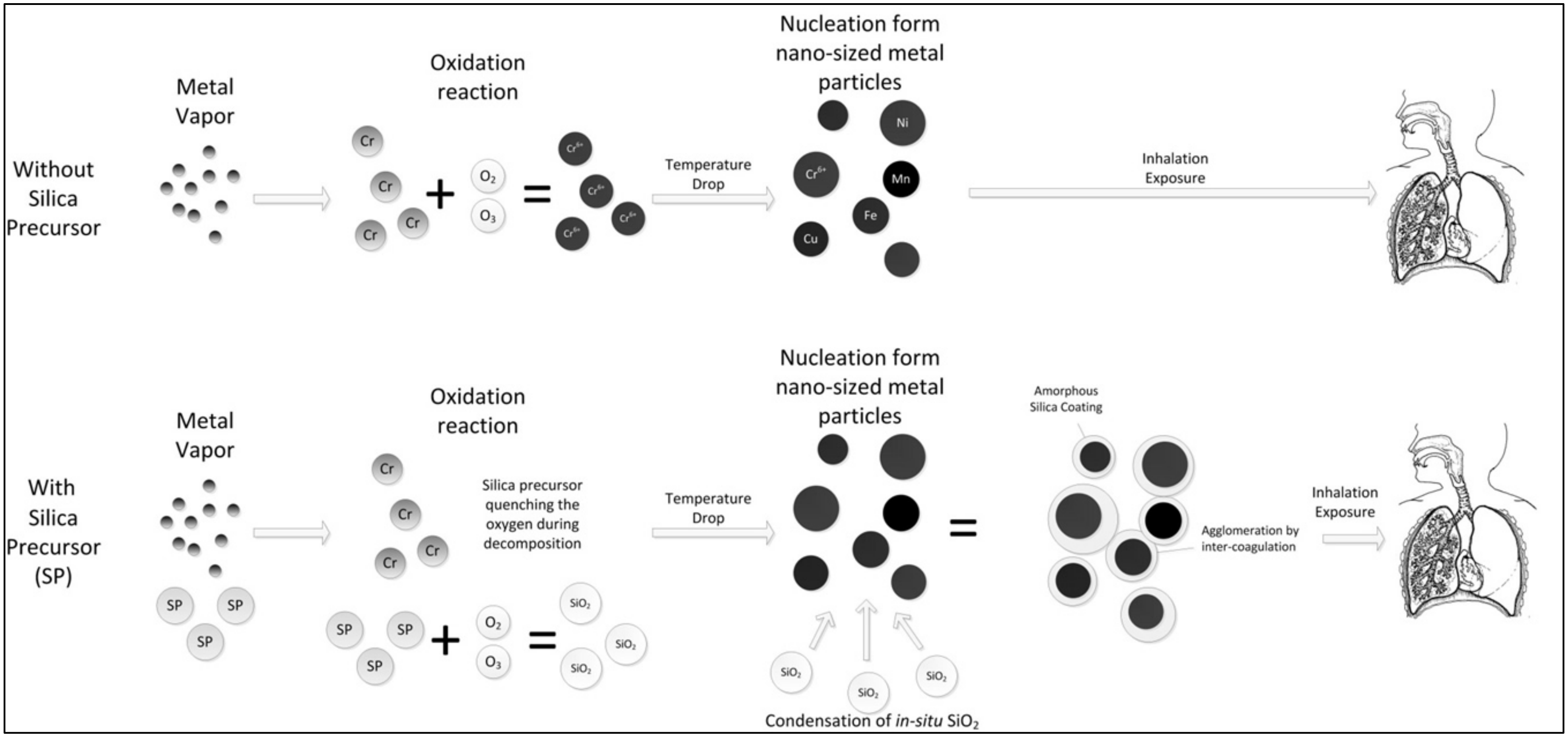

Figure 1. Diagram demonstrating the mechanism of silica precursor technology

3.0 PERFORMANCE OBJECTIVES

The performance objectives include:

- evaluate the reduction of Cr^{6+} in welding fumes
- determine silica coating efficiencies on metal particles
- measure particle size growth resulting from the silica network
- test the reduced biotoxicity of treated welding fumes
- assess the impact of the technology on welding operation
- examine the mechanical properties of the welds generated by silica precursor technology

All of the performance objectives were achieved during the demonstration, and are summarized in Table 1.

Table 1. Demonstration performance objectives and results

Performance Objectives	Data Requirements	Success Criteria	Results
Quantitative Performance Objectives			
Reduction of Cr^{6+} in welding fume	Cr^{6+} concentration in welding fume compared to baseline in the laboratory and during field demonstrations	Over 90% reduction efficiencies under all conditions; satisfying OSHA PEL	Met the criteria
Qualitative Performance Objectives			
Silica coating on metal particles	TEM images, silica coating efficiencies based on test plates joined in the laboratory and field	Visual evidence and bulk analysis of silica coating on particles	Met the criteria
Growth of welding fume particle size	SMPS particle size distribution	Mode size of welding fume particles under TMS condition shifted to the larger size range	Met the criterion
Reduced biotoxicity of welding fume	*E. coli* colony forming units, 50% lethal logarithmic concentrations based on welding fumes generated during welding in the laboratory	Growth rate of *E. coli* exposed to TMS-treated particles being higher compared to baseline welding fumes	Met the criterion
Minimum impact on welding operation	Response from welders participating in the field demonstration	Ease of implementation, no alteration of welding operation process	Met the criterion
No change in weld mechanical quality	Radiographic analysis, macro- and micro-chemical analysis, transverse tensile and bend tests based on test plates	No deterioration of weld quality with TMS added compared to baseline weld	Met the criterion

4.0 SITE/PLATFORM DESCRIPTION

4.1 TEST PLATFORM/FACILITIES

Tooele Army Depot (TEAD) was selected as the test site for the field demonstration. TEAD is an active ammunition storage site responsible for shipping, storing, receiving, inspecting, demilitarizing, and maintaining training and war reserve conventional ammunition. This facility also performs a significant amount of welding with stainless steel base metals. TEAD engineers and technical staff design and manufacture ammunition-peculiar equipment (APE) used in maintenance and demilitarization of munitions for DOD. The "peculiar" equipment is typically one-of-a-kind or small batches of equipment to fill a specific need in demolishing outdated or unused ammunition.

4.2 PRESENT OPERATIONS

The TEAD technical staff and welders use conventional welding technology to maintain and demilitarize the APE. The welding operations in Type 304 steel are performed using shielded metal arc welding (SMAW), gas metal arc welding (GMAW), and gas tungsten arc welding (GTAW) processes with conventional welding consumables E308L (SMAW) and ER308L (GMAW and GTAW). In some years, TEAD may use up to 500 pounds of consumables for 304 base metals; in other years, the usage may be minimal.

Conventional welding with stainless steel presents obstacles for compliance with the OSHA Hexavalent Chromium Standard, especially in enclosed spaces. This demonstration intended to replace this conventional technology with the novel silica precursor welding technology to reduce on-site welders' exposure to welding fumes and decrease the amount of HAPs potentially released into the environment. The demonstration verifies the laboratory results and includes a collection of welders' opinions about the implementation of this technology (such as ease-of-use issues).

4.3 SITE-RELATED PERMITS AND REGULATIONS

Currently there is no site-specific permit or regulation for implementing this technology.

5.0 TEST DESIGN

A laboratory study was first conducted to optimize the process. This was followed by a field test based on the knowledge gained from laboratory testing.

5.1 LABORATORY STUDY

The welding-fume generation and sampling system followed the American Welding Society (AWS) fume hood design recommended in Method F1.2-1999 [22]. A conical chamber and a Lincoln Power MIG 140C welder were used to produce welding fumes (Figure 2). The base metal was placed on a rotating turntable inside the hood to maintain a constant weld speed, while the ER308L stainless steel wire were fed by the welding gun.

Figure 2. Fume chamber and welding machine **(Photo by Jun Wang)**

Fumes from the baseline study that used 75% Ar/25% CO_2 as a shielding gas (i.e. no TMS introduced) were collected to determine emissions of Cr^{6+} during normal welding operations. This scenario represented the standard welding method currently used by many DOD welders. There were two methods of introducing TMS into the shielding gas (75% Ar/25% CO2):

- the premix
- insulated double-shroud torch (IDST)

In the premix mode, the welding torch was modified to allow injection of TMS by insertion of a Y-fitting to connect the torch and the gas hose. In the IDST mode, a newly designed torch (Figure 3) was used to allow separate flows of shielding gas and TMS carrier gas.

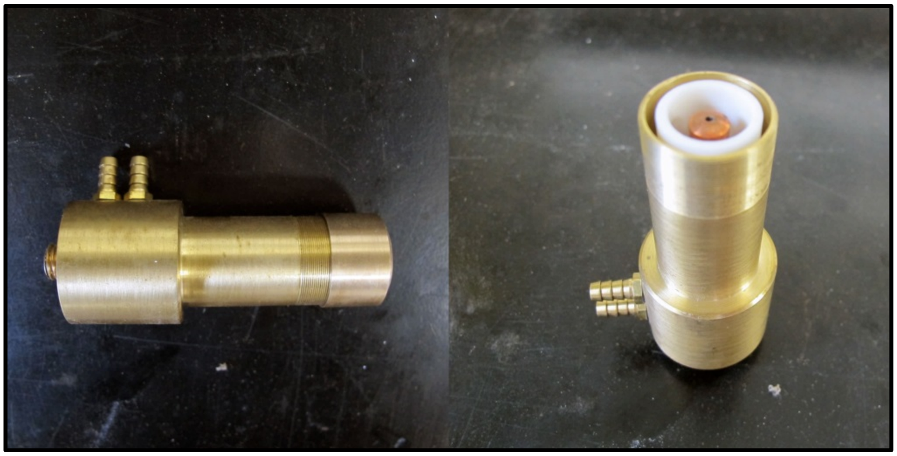

Figure 3. The IDST torch (Photo by Jun Wang)

Ion chromatography (IC) was used to measure the soluble hexavalent chromium species, chromate (CrO_4^{2-}). Sample extraction for IC analysis followed NIOSH Method 7604 [23]. X-ray photoelectron spectroscopy (XPS) is a non-destructive analytical process that allows examination of the valance state of Cr in the range of penetration depth of an X-ray. The XPS system gives the relative ratio of Cr^{6+}/Cr^{3+} in the welding fume. Analysis of total metals (Fe, Cu, Cr, Ni, and Mn) was carried out with inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Transmission electron microscopy (TEM) was used to observe SiO_2 coating formed on fume particles and particle morphology. A scanning mobility particle sizer (SMPS) was used to obtain aerosol-size distribution data.

A conservative method of quantifying the proportion of metals encapsulated inside the silica shell was developed [24]. Aqua regia was able to effectively dissolve metal particles not trapped in the silica shell. A mixture of HNO_3/HF was found to be an aggressive digestion method for metal particles even with silica coating. The mass difference between the results obtained from these two digestion methods was therefore used to calculate the silica coating efficiency.

E. coli bioassay was used to study the toxicity of welding fume. Colony-forming units (CFU) were measured per milliliter. The results from the baseline and TMS-added welding fume particles were compared.

5.2 FIELD TEST

The field demonstration was performed at TEAD, Tooele, UT in August, 2011. Two types of sampling were conducted: low-flow sampling and high-flow sampling. The area used for welding was a room at one end of a maintenance building that had two main doors, a double door on an inside wall, a large roll-up door on an exterior wall, and two windows. The exterior doors and windows were closed during testing. The interior doors were sealed off with duct tape and plastic sheeting. All doors were closed and openings taped shut, and no person was allowed to go in or out of the room during welding.

Low-flow sampling included three different pieces of equipment running concurrently. The sampling system incorporated a portable LEV collector (Figure 4a), an Electrical Low Pressure Impactor (ELPI) and a Grimm Aerosol Spectrometer. The sampling inlet was on the hood face, as shown in Figure 4b. Occupational Health and Safety (OSH) testing following the NIOSH Method 7300 included pumps placed in the near field and far field.

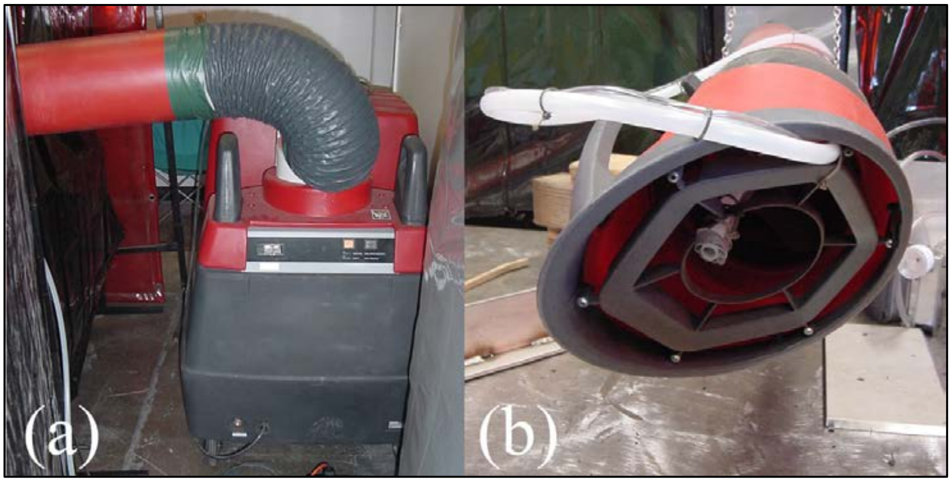

Figure 4. (a) Lincoln LEV collector and (b) sampling inlet on hood face **(Photo by Kathleen Paulson)**

The mass of Cr^{6+} and other elements (Ar, Cd, Co, Cr, Ni, Mn, Cu, Zn, Fe, Pb) was determined using inductively coupled plasma – mass spectroscopy (ICP-MS), and concentrations of these metals in the air were estimated using the sampling flow rate. In addition to metals, the concentration of respirable amorphous silica was measured.

In addition to the low-flow sampling, the University of Florida team conducted a high-flow sampling to collect full samples. A high-volume pump was used in the field to collect the fume particles. The welding fume particles were sampled using a pump mounted next to the welder (Figure 5). All the filter samples were shipped overnight to the University of Florida lab and digested the next day. The protocols for the analysis of Cr^{6+} and total metals remained the same as those used in the laboratory test.

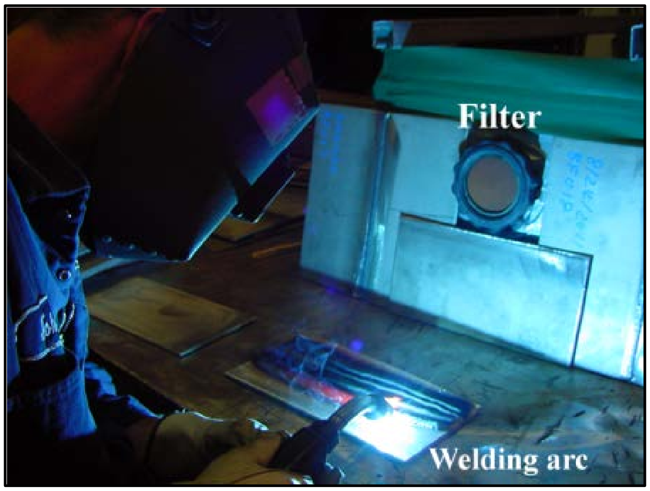

Figure 5. Setup of the pump and welder in high-flow sampling

A total of six plates were sent to the Naval Surface Warfare Center Carderock Division for weld-quality test evaluation. The evaluation consisted of radiographic tests, surface chemical analysis, and transverse tensile testing.

All the experiments described in the test design were repeated at least three times to ensure statistical quality. All data collected in the laboratory tests and the field demonstration tests were subjected to statistical examination using SAS 9.3 software at the University of Florida. The comparison of baseline welding and welding with TMS technology was done by the analysis of variance (ANOVA) method.

6.0 PERFORMANCE ASSESSMENT

6.1 LABORATORY TEST

Figure 6 shows the Cr^{6+} concentration at three primary shielding gas flow rates (20, 25, 30 liters per minute [Lpm]) for both the premix mode and the IDST mode. Regarding the premix mode, mixing about 4.2% of tetramethylsilane (TMS) carrier gas into the primary shielding gas led to an over 93% reduction of Cr^{6+} concentration to 4.2 µg/m^3, which was below the new OSHA standard (5 µg/m^3) [25]. However, the high removal only occurred with the high primary shielding gas flow rate, i.e., 30 Lpm. The shielding gas could not effectively disperse the heat generated from the welding process and insulate the heat transfer to the welding gun. Therefore, the silica precursor that was premixed upstream decomposed before reaching an effective position (i.e., the welding arc zone). A large amount of silica powder was found deposited inside the welding gun under these conditions. These results suggest it would be best to avoid the premix mode in favor of effectiveness under all conditions.

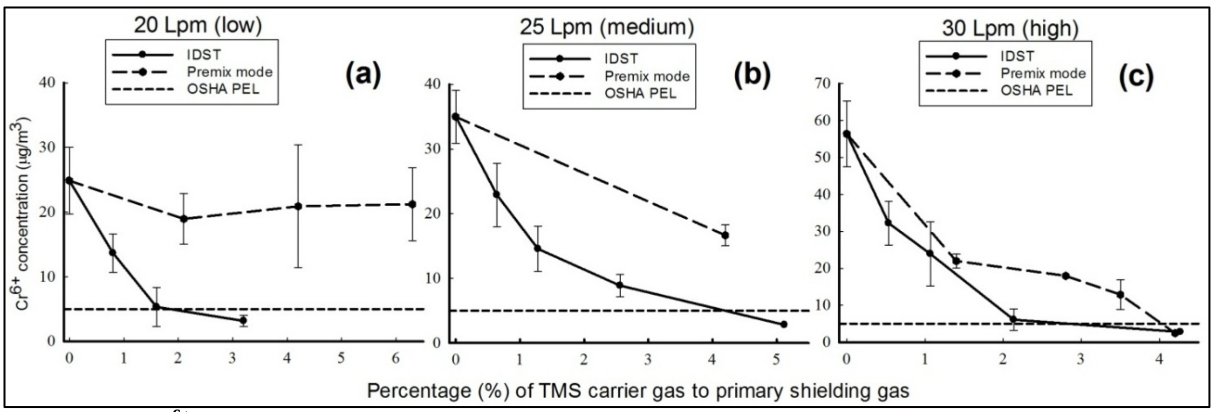

Figure 6. Cr^{6+} concentration as a function of the ratio of TMS to different shielding gas flow rates

The IDST can avoid excess thermal energy from being transferred to the silica precursor. Figure 7 shows the cross-sectional sketch of the new IDST. The precursor flows separately from the primary shielding gas, which is a carrier of heat.

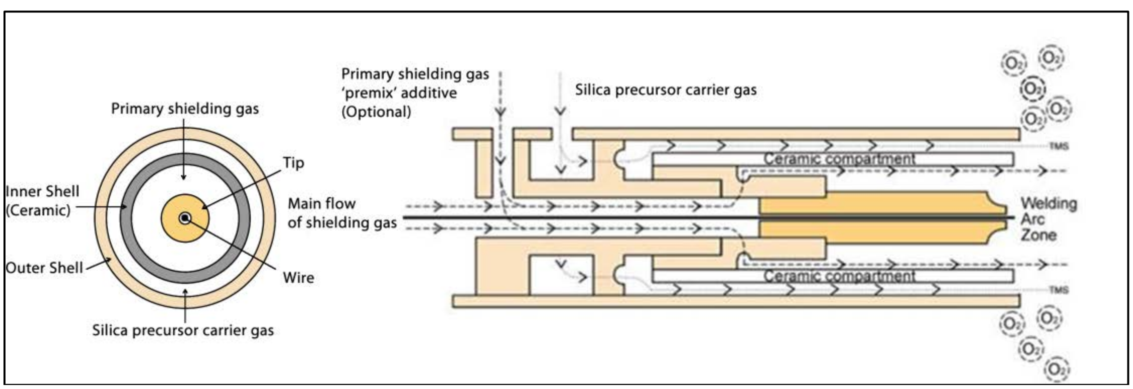

Figure 7. Schematic design of the IDST

Experiments using the IDST showed the silica precursor was able to reduce Cr^{6+} over 90%, which satisfied the OSHA PEL under all flow-rate conditions (Figure 6). Furthermore, the XPS results confirmed that Cr^{6+} inside the silica shell was reduced with a gradually increasing TMS ratio. Visual inspection did not find any silica powder deposited on the ceramic compartment and the inner side of the welding torch. This is direct evidence of the IDST's ability to eliminate premature reaction of the silica precursor inside the welding gun.

Increasing silica coating efficiency using IDST was also expected. The premix mode showed about 14 to 38% of the metals encapsulated, depending on the flow rate. The relatively low coating efficiency was caused by a mismatch of metal vapor's nucleation and silica formation, i.e., premature decomposition.

Figure 8 displays the TEM imagery of welding-fume particles under various conditions. Figure 8a show the welding-fume particles generated from baseline condition. Figures 8b-c show the welding-fume particles generated from 30 Lpm primary shielding gas and 0.64 Lpm TMS carrier gas flow with silica coating efficiency (SCE) of 76±7.9%. The images showed a silica-encapsulated metal agglomerate, with a clear boundary between the amorphous silica layer and its metal components. Figure 8d shows the welding-fume particles generated from 30 Lpm primary shielding gas and 0.96 Lpm TMS carrier gas flows with SCE of 43±9.0%. The particles are more randomly arranged, due to the high quantity of welding-fume particles generated and the possibly poor mixing interaction between the silica vapor and metal particles.

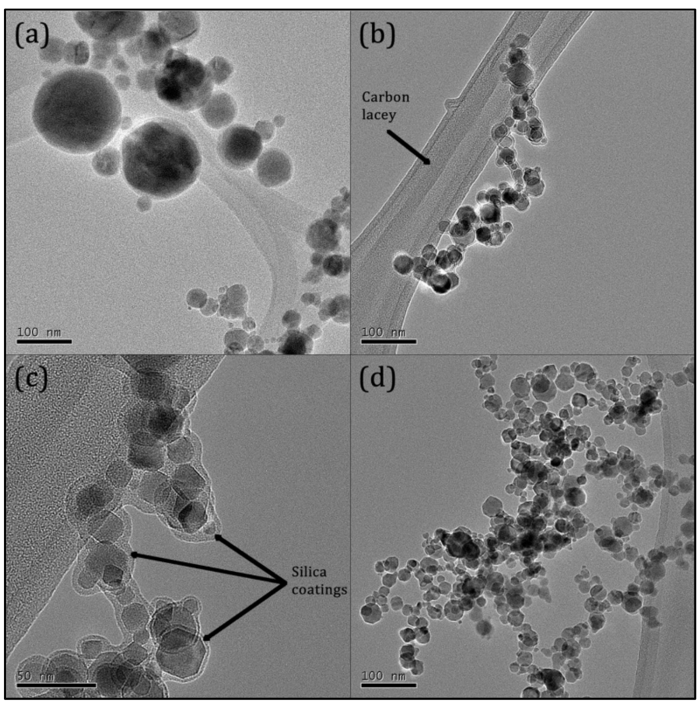

Figure 8. TEM images of different conditions of welding-fume particles

The silica precursor technology also increased fume-particle size from a mode (peak) of 20 nm under the baseline conditions to a mode of 180 to 300 nm when TMS was added in all shielding gas flow rates tested. SiO_2 particles formed in the process scavenged nano-sized fume particles through inter-coagulation. These results demonstrate the ability of vapor-phase silica precursor to reduce the health risks posed by welding fumes through agglomeration of nano-particles thus preventing less deep lung penetration.

The biotoxicity study of fume particles was conducted to evaluate the reduction of toxicity by the silica precursor technology [26]. For *E. coli* exposed to fume particles generated in TMS-injected shielding gas, the growth rate was much higher than in baseline cases with the same particle concentration. The 50% lethal logarithmic concentrations (LLC_{50}) were 823, 1605, and 1800 mg/L for baseline, 2%, and 4.2% TMS additive, respectively ($p<0.005$). These results indicated that adding TMS to the shielding gas could generate fume particles with lower biotoxicity.

6.2 FIELD TEST

The results from the low-flow sampling were limited due to insufficient fume mass collection. The concentration of Cr^{6+} in most samples was lower than OSHA PEL (5 µg/m^3) regardless of whether it was a baseline or TMS-injected sample. The variation between samples was relatively large (coefficient of variance > 1). However, reduction of Cr^{6+} and metals by TMS technology was still observed by use of ANOVA. The average Cr^{6+} mass collected during baseline and TMS-injected conditions was 0.56 and 0.23 µg, respectively, with about 59% reduction ($p<0.09$). Concentrations of amorphous silica in the environment were all below the detection limit for both baseline and TMS-injected conditions. The combustible gas monitor did not detect any fire hazard at any time during demonstration. These data all show that the hazard of using TMS in the welding process was minimal.

The results of the high-flow sampling in Figure 9 clearly show that the silica precursor technology was capable of reducing Cr^{6+} exposure below the OSHA PEL with > 90% Cr^{6+} reduction efficiency. The mean estimated Cr^{6+} exposure of the baseline condition was 9.77 µg/m^3, which was higher than the OSHA PEL. Because the TMS injected samples had concentrations below the method detection limit (0.33 mg/L), the mean Cr^{6+} exposure was estimated to be 1.07 µg/m^3 (i.e. the method detection limit) using the conservative estimation method, and the corresponding reduction efficiency was roughly 90%; 32.38% and 31.11% of metals were sealed inside the silica shell for the two tests conducted, respectively. These results support the hypothesis that the silica precursor technology, by scavenging oxygen species and sealing metals in an amorphous silica layer, has the potential to lower welders’ exposure to hazardous metals.

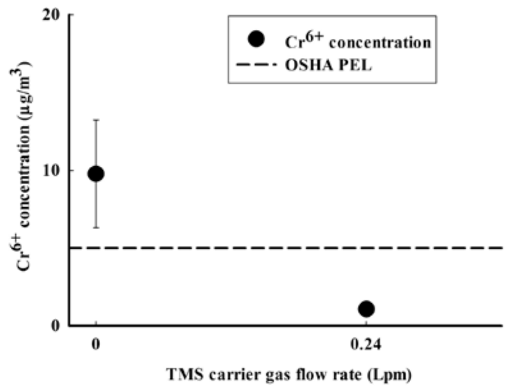

Figure 9. Cr^{6+} concentration measured in the field

The welder in the field also commented on the ease of the change when welding with the TMS additive rather than conventional welding. The arc transfer was identical, except TMS could burn as it came out of the torch. This effect could be minimized by setting the flow of TMS carrier gas appropriately. When the flow was too high, there was a very noticeable flame and the weld puddle was too hot. The welder recognized and adjusted the TMS carrier gas flow easily. The welder believed the TMS technology could be used with little to no change, and good quality welds could be obtained.

The chemical composition analyses of the baseline and TMS-injected samples are identical and within the standard limits. The macrostructures and microstructures of the three baseline plates revealed a typical welded metal and did not appear to contain any weld defects. The macrostructures of the TMS-injected plates were similar to those of the baseline plates. However, a crack at the interface between the weld metal (WM) and the heat affected zone (HAZ) appeared in one sample. The TMS addition, or problems with shielding gas, or improper welding technique might have caused gas pockets, which could have coalesced into a crack.

The results of the tensile tests of the welds are shown in Figure 10. The yield strength (YS) of the welds from the baseline and the TMS technology were identical, 44±1 kilo-pounds per square inch (ksi) (Figure 10a). Meanwhile, the (UTS) of the welds from the baseline and the TMS technology were 83±4.3 ksi and 77±8.1 ksi, respectively, with no statistical difference ($p>0.1$) (Figure 10b). Figure 10c shows the comparison of average elongation of welds from the baseline and the TMS technology. Again, the elongation values showed no statistical difference ($p>0.1$). The AWS requirement for ER 310 stainless steel is also displayed. The AWS minima for UTS and elongation for filler materials are marked as dash lines in Figures 10b and 10c. However, it should be noted that the AWS minima for standard filler materials are provided just for reference purposes and they should not be directly compared to the values measured from welded materials. The non-homogeneity of the welded materials (WM, HAZ and base metal) naturally results in lower values compared to those of the uniform standard materials. For YS, there is no AWS minimum due to the difficulty in obtaining valid transverse yield strength.

As both the baseline and the TMS samples were lower than the AWS minimum, welder inexperience working with a new welding shielding gas additive likely is a major factor contributing to the imperfect welds. If not from the statistical aspect, the result indicated that the TMS technology reduced tensile strength in some samples.

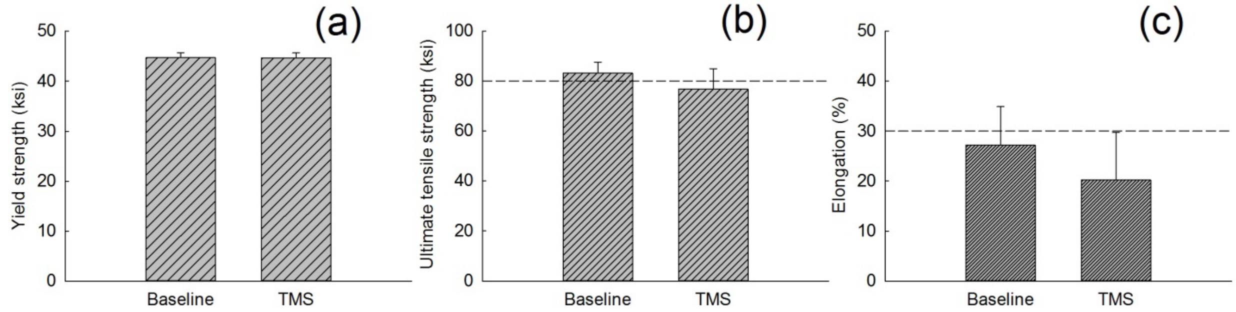

Figure 10. (a) Yield strength (YS); (b) ultimate tensile strength (UTS); (c) elongation of welds generated with baseline and the TMS technology.

In summary, while the TMS technology did not statistically deteriorate the mechanical quality of the welds, optimization of different welding parameters to achieve better tensile property certainly should be considered.

7.0 COST ASSESSMENT

The cost assessment intended to compare three baseline welding processes and welding using the TMS technology. A major assumption of this analysis is that the TMS additive will allow for the use of conventional ventilation systems.

7.1 COST MODEL

The cost model used was developed in 2006 under SERDP Project PP-1415, *Development of Chromium-Free Welding Consumables for Stainless Steels*. Some aspects of this approach were used to assess and compare the costs associated with the TMS additive vs. the use of standard (argon) shielding gas. Ten different combinations of joint type and industry sector were evaluated. These same combinations were evaluated to assess costs as a result of using the TMS technology. The industry sectors selected were shipbuilding, transportation and storage tanks, and general fabrication. The joint designs included V-groove butt welds between both pipe and plate configurations, as well as T joints with fillet welds.

7.2 COST ANALYSIS AND COMPARISON

The criteria developed in PP-1415 were used for the various GMAW joints with the additional costs associated with the three TMS approaches included. The unit costs of each scenario are listed in Table 2. These costs were then compared to costs of producing the same joints with standard shielding gas (argon). Scenario 1 represented the mixing of TMS at the torch. Scenario 2 used customized TMS cylinder gas, where the gas was supplied from the customized gas department of Airgas, a gas supply company. Scenario 3 was similar to Scenario 2, but with the estimated reduced cost of TMS cylinder gas once it is commercially available and in high-volume production ("commercial TMS cylinder gas").

Table 2. Unit costs used in the cost model

	Unit price	Consumption rate	Cost per minute
Scenario 1			
Primary shielding gas (Ar/CO_2)	\$27/300 ft^3	29 Lpm	0.0922
Carrier gas (Ar)	\$25/300 ft^3	1 Lpm	0.00294
TMS	\$65.16/100 mL	0.02 mL/min	0.0130
Scenario 2			
Primary shielding gas (Ar/CO_2)	\$27/300 ft^3	29 Lpm	0.0922
TMS premix cylinder gas	\$1,264/44 L	1 Lpm	28.7
Scenario 3 (Commercial product of cylinder gas)			
Primary shielding gas (Ar/CO_2)	\$27/300 ft^3	29 Lpm	0.0922
TMS premix cylinder gas	\$205/300 ft^3	1 Lpm	0.0241

The results found that using TMS mixing at the torch would slightly increase costs, while using customized TMS cylinder gas would dramatically increase costs. The estimated commercial TMS cylinder gas can reduce the costs to the same level as TMS mixing at the torch. TMS in the cylinder would be more convenient to end users than the other means. While customized TMS cylinder gas is already available, currently it is only available through custom order. The result suggested that costs would be greatly reduced once the TMS precursor technology becomes widely adopted in the welding community, and TMS gas in cylinders becomes a commonly available commodity.

When OSHA established the new ventilation requirements for reducing exposure to hexavalent chromium it stated the primary methods for reducing such an exposure would be through retrofitting the ventilation system. Lincoln Electric provided the ventilation system quotes for this analysis. In summary, the initial cost associated with purchasing ventilation equipment to meet the new OSHA standard for a 200- by 100-ft welding shop with 36 welders was approximately $700,000. The recurring costs were estimated to be $50,000/year. In comparison, the total estimated cost for a ventilation system not subject to the new OSHA requirement was $410,000, and the recurring costs were estimated at $20,000/year. This analysis indicated requirements for approximately $290,000 in additional funding to purchase ventilation equipment, and $30,000/year in additional expenses associated with conforming to the new OSHA standard for a welding shop of this size.

For the purposes of better understanding the financial impact of the OSHA hexavalent chromium lower exposure requirement versus the additional costs associated with the TMS shielding gas technology, six scenarios involving the two welding shop sizes were compared. The results are summarized in Table 3.

Table 3. Summary of the cost comparison

Scenario	Weld shop size	Mixing mode of the TMS technology	Initial cost of the TMS technology	Annual recurring cost of the TMS technology	Ventilation cost without retrofitting the welding technology
1	200' x 100'	Mix at the torch	$109k	$59k	$290k
2		Customized gas cylinder	$44,000k	Insignificant	Insignificant
3		Commercial gas cylinder	$126k	$76k	$290k
4	60' x 30'	Mix at the torch	$37k	$20k	$62k
5		Customized gas cylinder	$15,000k	Insignificant	Insignificant
6		Commercial gas cylinder	$42k	$25k	$62k

In summary, using the model from SERDP PP-1415(45) to assess the additional costs of the TMS in various welding processes, the general material cost was calculated to increase by 3.8%. The cost of the shielding gas containing TMS was $0.6 per ft of weld. This cost does not include the initial capital cost of the IDST, which might vary significantly from laboratory phase to industrial bulk production. The costs of implementing the silica precursor technology are comparable to those of other control technologies such as local exhaust ventilation (LEV) and on-gun extraction.

8.0 IMPLEMENTATION ISSUES

One potential implementation concern is the safe handling of TMS. TMS is a flammable and volatile liquid. High concentration of TMS vapor may cause flash fires or explosions in oxidizing environments. Exposure to TMS may cause skin, eye, and respiratory tract irritation although the toxicological properties of TMS have not been fully investigated. We carried out a calculation of TMS concentration in a typical room with the worst-case scenario in which all the TMS has leaked into the air without forming silica—the TMS concentration in the tent/room would be 5.2 ppm. The value is orders of magnitude lower than the TMS lower flammable limit/lower explosion limit (LFL/LEL) of 1%. It should be noted this calculation is based on the worst case scenario, which is unlikely to occur. A ventilation system is recommended in the field to reduce accumulated TMS concentration, other gases, and welding metal emissions.

Several members of the ESTCP Review Board expressed concern about possible long term effects of amorphous silica coated particles in the pulmonary and gastric system. The team recommends further toxicological studies beyond the *E. coli* testing already done, such as genotoxicity, dissolution assessment, cytotoxicity, and dermal irritancy.

Despite the small number of weld tests in the mechanical quality test, the result suggests there is room for improving TMS technology to achieve higher weld quality. The weld quality of both baseline and TMS technology samples were lower than the minimum required by the standard for uniform metals indicating problems could be partially due to welder issues.

Future work on further promoting the applicability of the TMS technology includes the following:

- An in-depth experimental and modeling study of the welding process (heating, metal transfer, pool cooling, etc.) while welding with TMS technology
- Conducting a more comprehensive mechanical quality test with more welds and welders involved

Once the optimization and improvement of the TMS technology is finalized, the technology transfer process can begin. Several shielding gas companies (Airgas, Praxair, Air Liquide) are willing to adopt any new and demonstrated shielding gas recipe as long as the technology has a viable market. However, due to the fact that this project was unexpectedly terminated before the optimization and improvement could be achieved, the technology transfer will take a different path.

The University of Florida is pursuing other applications for the TMS technology including using TMS as a catalyst to control mercury in fly ash generated during incineration processes. Understanding the behavior of TMS in these systems may promote better understanding of how it behaves during welding operations and will increase the knowledge of how TMS can be handled safely in industrial operations.

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